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# <Division of Materials Chemistry>Polymer Controlled Synthesis

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# Division of Materials Chemistry – Polymer Controlled Synthesis –

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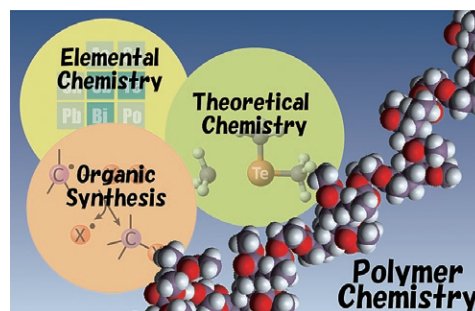
Centre for Advanced Macromolecular Design (CAMD), The University of New South Wales, Australia, 20 December

## Scope of Research

Our research focuses on creation of new organic molecules which would become key reagents and materials for future science and technologies. Furthermore, we have been developing new organic and polymeric materials based on our tailor-made molecules. One such topic is the development of new living radical polymerization method utilizing heavier heteroatom compounds as controlling agents. The other topic is the synthesis of cycloparaphenylenes, hoop-shaped  $\pi$ -conjugated molecules, based on new synthetic strategy. We also study various polymer condensed states by both static and dynamic methods to understand the relation of physical properties and structures.

### KEYWORDS

Organic Synthesis      Living Radical Polymerization      Conjugated  $\pi$ -molecules  
Polymer Synthesis      Polymer Properties



## Selected Publications

Nakamura, Y.; Arima, T.; Tomita, S.; Yamago, S., Photoinduced Switching from Living Radical Polymerization to a Radical Coupling Reaction Mediated by Organotellurium Compounds, *J. Am. Chem. Soc.*, **134**, 5536-5539 (2012).

Tosaka, M.; Senoo, K.; Sato, K.; Noda, M.; Ohta, N., Detection of Fast and Slow Crystallization Processes in Instantaneously-Strained Samples of cis-1,4-Polyisoprene, *Polymer*, **53**, 864-872 (2012).

Iwamoto, T.; Watanabe, Y.; Sakamoto, Y.; Suzuki, T.; Yamago, S., Selective and Random Syntheses of  $[n]$ Cycloparaphenylenes ( $n = 8-13$ ) and Size-Dependence of Their Electronic Properties, *J. Am. Chem. Soc.*, **133**, 8354-8361 (2011).

Iwamoto, T.; Watanabe, Y.; Sadahiro, T.; Haino, T.; Yamago, S., Size-Selective Encapsulation of  $C_{60}$  by  $[10]$ Cycloparaphenylene. Formation of the Shortest Fullerene-Peapod, *Angew. Chem. Int. Ed.*, **50**, 8342-8344 (2011).

Kayahara, E.; Yamada, H.; Yamago, S., Generation of Carbanions via Stibin-Metal and Bismuthine-Metal Exchange Reaction and Its Applications to Precision Synthesis of  $\omega$ -End Functionalized Polymers, *Chem. Eur. J.*, **17**, 5272-5280 (2011).

Nakamura, Y.; Kitada, Y.; Kobayashi, Y.; Ray, B.; Yamago, S., Quantitative Analysis of the Effect of Azo Initiators on the Structure of  $\alpha$ -Polymer Chain Ends in Degenerative Chain Transfer-Mediated Living Radical Polymerization Reactions, *Macromolecules*, **44**, 8388-8397 (2011).

## Photoinduced Switching from Living Radical Polymerization to a Radical Coupling Reaction Mediated by Organotellurium Compounds

Modulation of the reaction pathway using external stimuli has been a significant challenge in organic and polymer syntheses, because such methods would considerably expand the structural diversity of products from a limited number of precursors. Although a variety of chemical stimuli have been used for this purpose, physical stimuli, such as thermal and photochemical stimuli, like those used in the pericyclic reactions, are attractive due to their “green” character.

We have already reported that organotellurium-mediated living radical polymerization (TERP) possesses several synthetic advantages such as high monomer versatility, high compatibility toward functional groups and solvents, and ease of the living-end transformation for the synthesis of block copolymers and end-functionalized polymers. While expanding the synthetic applicability of TERP to dienes, we found that the reaction pathway can be selectively switched from LRP to a radical-coupling reaction (RC) by using photostimuli (Figure 1). Structurally well-defined telechelic polyisoprenes and ABA-triblock copolymers were prepared by successive organotellurium-mediated living radical polymerization (TERP) under thermal conditions, followed by a polymer-end radical coupling reaction under photoirradiation.

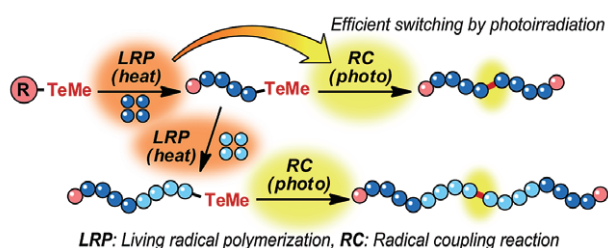


Figure 1. Switching of reaction pathway.

## Formation of the Shortest Fullerene-Peapod

Cycloparaphenylenes (CPPs) are hoop-shaped  $\pi$ -conjugated molecules in which paraphenylene units are linked in a cyclic manner (Figure 2). They represent the simplest structural unit of armchair carbon nanotubes. Based on the analogy to layered carbon networks with curved surfaces, the concave cavity of the CPPs should act as a host for  $\pi$ -conjugated molecules with a convex surface, such as fullerenes. Such a host–guest complex would be a suitable model for elucidating convex–concave  $\pi$ – $\pi$  interactions. We found that [10]CPP selectively encapsulated  $C_{60}$  forming the shortest fullerene-peapod, [10]CPP  $\supset C_{60}$ , among several CPPs prepared by the method we have developed (Figure 3). This finding opens the possibility of utilizing CPPs as size- and shape-selective host molecules for various guest molecules, such as higher fullerenes, metallofullerenes, and carbon nanotubes. Such complementary host–guest chemistry will be useful for the size- and shape-selective separation of higher fullerenes and carbon nanotubes.

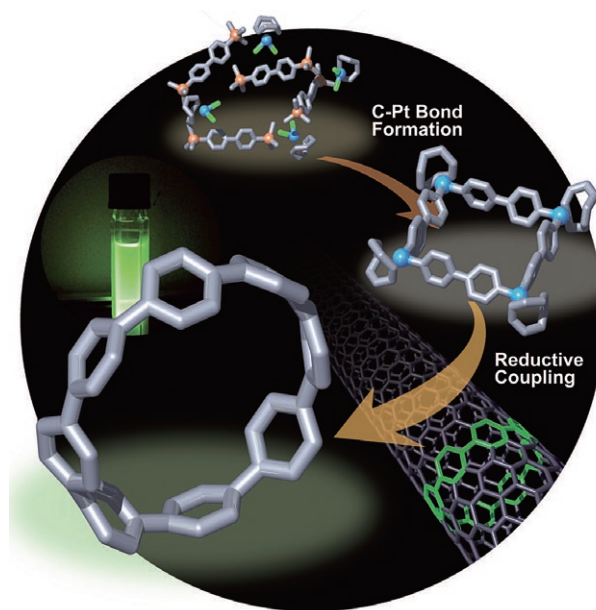


Figure 2. Synthesis of CPP.

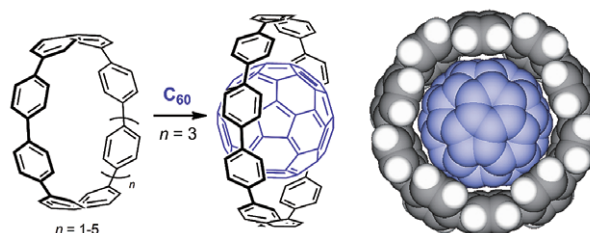


Figure 3. Formation of the shortest fullerene-peapod.